

MANGANESE DIOXIDE-COATED ACTIVATED ALUMINA – A MEDIUM FOR OXIDATION/ADSORPTION OF ARSENIC IN GROUND WATER

*A Thesis Submitted
in Partial Fulfillment of the Requirements
for the Degree of*

MASTER OF TECHNOLOGY

in

Environmental Engineering and Management

by

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to the

DEPARTMENT OF CIVIL ENGINEERING

Indian Institute of Technology, Kanpur

May, 2001

17 JUL 2001/CE

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ABSTRACT

In a laboratory study, manganese dioxide-coated activated alumina (MDAA) was prepared by the incipient wetness impregnation method, characterised and tested as a medium for the removal of arsenic from ground water. In a preliminary downflow column test, MDAA was found to be a more effective medium than activated alumina (AA) for the removal of As(III), and for this medium, the effluent arsenic at breakthrough contained both As(III) and As(V), indicating oxidation of As(III) to As(V) by the manganese dioxide coating. Batch kinetic tests showed that in comparison to AA, both As(III) and As(V) were removed (oxidised/adsorbed) at a faster rate on MDAA, the difference in the rates being significantly higher for As(III). For both AA and MDAA, rate of removal (oxidation/adsorption) of As(III) and As(V), when present together, was intermediate to the rates obtained when As(III) or As(V) was present alone in the water. In three cycles of downflow column test [medium depth 200 mm; empty bed contact time 20 min; influent arsenic 1.0 mg/L (0.6 mg/L As(III); 0.4 mg/L As(V))] MDAA was found to be a better medium for arsenic removal, with breakthrough bed volumes at the WHO guideline value of 0.01 mg/L for arsenic in drinking water being in the range 695-825 for MDAA and 485-580 for AA. For AA, the effluent arsenic at breakthrough was in the form of As(III), whereas for MDAA, both As(V) and As(III) were present. During regeneration, recovery of the adsorbed arsenic was in the range 88-84% for AA and 89-86% for MDAA. Based on the results of the study, MDAA appeared to be a more effective medium for the removal of both As(III) and As(V) from ground water.

ACKNOWLEDGEMENT

I take this opportunity to express my sincere regards and gratitude for my thesis supervisor Dr. Malay Chaudhuri. His immense patience, endurance and meticulous handling of problems encouraged me and made my stay worthwhile at the institute. He has been a perennial source of inspiration and information for me. I am indeed fortunate to get an opportunity of working with him.

I am also indebted to my teachers, Dr. Saumyen Guha, Dr. Purnendu Bose, Dr. Mukesh Sharma, Dr. D.K. Ghosh, Dr. V. Tare and Dr. B. Rath for their kind cooperation and support throughout my stay in this department.

The joyful company of my classmates and friends, Kaka, Soni, Brajesh, Anubha, Mukul, Sarna, Rakesh, Sujata, Shailesh, Souvik, Amit and Pramod will always remind me of my memorable days as a student at I.I.T., Kanpur. I also acknowledge the affection given to me by the junior batch of students, especially Anuj, Raman, and Akash. I am also grateful to Patidarji, Shuklaji, and Satvatji for their help and advice in the laboratory.

I am also grateful to Mishraji, Nekramji, R.B. Lalji, Yadavji and Vijayji for their ready help and cooperation in the laboratory.

I shall always remain indebted to my parents for their constant support, inspiration and understanding without which I wouldn't be what I am today. Last but not the least, I would like to thank Shweta and Gaurav for the help they extended to me.

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1. INTRODUCTION

The presence of toxic substances in ground water poses a major threat to a large number of people as in many countries ground water is the primary source of drinking water. Arsenic, in particular, presents a significant threat to human health as it is a well-known toxic element and a documented human carcinogen. The World Health Organization (WHO) has established a provisional guideline value of 0.01 mg/L for arsenic in drinking water (WHO, 1993).

Most of the reported arsenic problems in water supplies are found in ground waters containing geogenic arsenic in elevated concentrations. Arsenic may also be an anthropogenic pollutant of ground and surface waters, derived from chemical wastes and wastewaters. It may not be retarded effectively in ground water movement by adsorption and can penetrate far into the saturated zone, in a manner similar to a conservative tracer.

Arsenic is a naturally-occurring element that ranks twentieth in abundance in the earth's crust, fourteenth in seawater, and twelfth in the human body (Woolson, 1975). High natural occurrence, combined with man-made sources, are responsible for increasing arsenic concentrations in ground waters. Arsenic occurs in both organic and inorganic forms, but the organic arsenic species are generally present in smaller amounts than the inorganic forms, arsenite and arsenate. Arsenite is the most toxic amongst the various forms of arsenic present in ground water and, therefore, even at a very low concentration, it is a threat to the community. High arsenic levels in ground water have been reported from many parts of the world, such as Argentina (Water, 2000), Bangladesh (Water, 2000), Canada (Grantham and Jones, 1977), Chile (Borogono et al.,

1977), China (Lianfang and Jianzhong, 1994), Japan (Terada, 1960), Mongolia (Water, 2000), Taiwan (Tseng et al., 1968) and USA (Feinglass, 1973). In India, arsenic concentration above 0.05 mg/L has been found in the ground water of eight districts of West Bengal covering an area of 38,000 sq km with a population of 38 million, and the maximum concentration of arsenic has been recorded as 3.7 mg/L (Mandal et al., 1998). In Bangladesh, arsenic concentration above 0.05 mg/L has been reported in tubewell waters in forty-one districts, and in twenty-one districts, people suffering from arsenic-induced skin lesions (melanosis, leuco-melanosis, keratosis, dorsum, non-petting oedema, gangrene and skin cancer) have been identified (Dhar et al., 1998).

In ground water, arsenic exists in two valency states, as trivalent anion [arsenite, As(III)] or as pentavalent anion [arsenate, As(V)]. As(V) is removed more efficiently than As(III) as the former exists as monovalent or divalent species, whereas As(III) predominantly exists as a neutral species (Gupta and Chen, 1978). Conventional water treatment involving coagulation with hydrolysing metal salts such as ferric sulfate, ferric chloride and alum, followed by settling and filtration is an effective method of removing arsenic from water (Buswell et al., 1943; Gullledge and O'Connor, 1973; Scott et al., 1995). Lime treatment (softening) with powdered coal additive has also been found to be effective in removing arsenic from water (Dutta and Chaudhuri, 1991). Due to ease of handling, sludge-free operation and regeneration capacity, fixed-bed techniques of ion exchange and adsorption are more suitable methods for arsenic removal.

For point-of-use treatment for arsenic removal, activated alumina in fixed-bed reactors has proved to be effective; however, As(V) has been found to be more effectively removed than As(III), and oxidation of As(III) to As(V) is necessary to

achieve high arsenic removal (Gupta and Chen, 1978). In theory, for enhancement of adsorption of a higher anion such as As(V), protonation of activated alumina is desirable (Clifford, 1990). In field and laboratory studies, alkali-acid pretreated activated alumina has proved effective in the removal of arsenic from ground water (Fox, 1989, Govind, 1999).

Based on the evidence of oxidation of arsenite by iron and manganese oxides, adsorption of arsenite and arsenate by iron hydroxide, and adsorption of arsenate by hydrous manganese oxide (Oscarson et al., 1981a, 1983; Pierce and Moor, 1980, 1982; Takamatsu et al., 1985), it appeared that granular iron or manganese oxide, or a porous supporting medium coated with iron or manganese oxide would serve as an effective medium for removing arsenic from water. Granular ferric hydroxide (Driehaus et al., 1998), iron oxide-coated sand (Joshi and Chaudhuri, 1996) and manganese dioxide-coated sand (Bajpai and Chaudhuri, 1999) media have been developed and found effective in removing arsenic from ground water. However, manganese oxides being more effective oxidants for As(III) than iron oxides (Oscarson et al., 1981a) and manganese dioxides (δ -MnO₂ and α -MnO₂) being most effective (Oscarson et al., 1981b), a manganese dioxide-based medium would be more effective for oxidation/adsorption of arsenic from ground water. In a recent study to examine in detail the oxidation/adsorption of arsenic by manganese dioxide-coated sand, Verma (2000) has reported that the cations present in ground water make the manganese dioxide surface positively charged and thus causing adsorption of As(V) and aiding further oxidation/adsorption of As(III), and that the sand matrix under the coating also plays a role in the adsorption of As(III) and As(V), suggesting that manganese dioxide (δ -

$\text{MnO}_2/\alpha\text{-MnO}_2$) coated on a supporting medium with high As(V) adsorption capacity, such as activated alumina, would be a more effective medium for the removal of arsenic, As(III) and As(V), from water.

The present study was undertaken with a view to developing a manganese dioxide-coated activated alumina medium and to examine the removal of arsenic, As(III) and As(V), from ground water by the medium vis-à-vis removal by activated alumina.

2. BACKGROUND INFORMATION

This chapter contains background information on the sources and occurrence of arsenic in water and the chemistry of arsenic in water followed by a brief description of its health effects and guideline value for arsenic in drinking water. The available methodologies for removing arsenic from water and the potential of iron and manganese oxides in removing arsenic from water have also been discussed.

2.1 Sources and Occurrence of Arsenic in Water

Arsenic is a commonly occurring toxic element in nature, and it is widely distributed in a large number of minerals. The highest mineral concentrations generally occur as arsenides of copper, nickel, iron, lead, silver, and gold, or as arsenic sulfide or oxide. Major arsenic-containing minerals are arsenopyrite (FeAsS), realgar (As_4S_4), and orpiment (As_2S_3). Arsenic ranks twentieth in crustal abundance in relation to other elements and the arsenic content of the earth's crust is 1.5-2.0 mg/kg (NAS, 1977). Arsenic in soil may originate from the parent materials that form the soil and from industrial waste discharges or agricultural use of arsenical pesticides. Oceans are also large reservoirs of arsenic with concentrations around 14 tons/m³ (Wenk, 1969). Deep-sea sediments have been found to have arsenic with concentrations ranging from few ppm to as much as 455 ppm (Gulledge and O'Connor, 1973).

Arsenic can enter the body via plant uptake from soils, by drinking arsenic-

contaminated surface or ground water, or by biomagnification as one moves up the food chain. The major starting point for introduction of arsenic into the environment is arsenopyrite, the most common arsenic-containing mineral (Bhumbla and Keefer, 1994). In nature, this arsenic-containing mineral undergoes oxidation and releases arsenic to water. Rapid oxidation of arsenic-containing minerals is also facilitated when geological materials from a reduced environment are brought to the surface of the earth during mining. Arsenic can also be released to the environment from the overburden material and from coal. A major portion of the arsenic found in natural water is derived from anthropogenic activities, such as use of arsenical pesticides, application of fertilizers, and industrial discharges such as wood preservatives, decolorisers in glass manufacturing, formulation of pigments and manufacturing of lead shots (Woodward, 1960; Browning, 1969). Arsenic undergoes reactions of oxidation-reduction, precipitation-dissolution, adsorption-desorption, and organic and biochemical methylation. All of these reactions control mobilisation and bioaccumulation of arsenic in the environment. Arsenic concentrations in water is governed more by arsenic speciation than by the total amounts of arsenic present and thus arsenic mobilisation in nature depends on the sources of arsenic, arsenic speciation, interactions of arsenic with soils, sediments, and geologic materials, and transformations and translocations by soil microbes and higher plants.

2.2 Chemistry of Arsenic in Water

Arsenic occurs in both inorganic and organic forms in water (Braman and Foreback, 1973; Crecelius, 1974). The main organic arsenic species, methylarsonic acid and dimethyarsinic acid, are generally present in smaller amounts in natural water than

the inorganic forms (WHO, 1981).

Arsenic chemistry in aquatic systems is quite complicated because the element can be stable in four oxidation states (+5, +3, 0, -3) under different redox conditions. In oxidized surface waters, arsenate (pentavalent) species (H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-}) are the stable forms; under moderately reducing conditions, the arsenite (trivalent) species (H_3AsO_3 , H_2AsO_3^- , HAsO_3^{2-}) become predominant. When sulfide is present, realgar (AsS) and orpiment (As_2S_3) occur as stable solids at pH values below approximately 5.5 and redox potentials (Eh) of about 0 volts, while HAsS_2 and AsS_2^- are the predominant aqueous species (Gupta and Chen, 1978). Elemental arsenic is thermodynamically stable at low Eh level with low solubility.

Arsenite, As(III), is oxidized to arsenate, As(V), in the presence of oxygen, chlorine or potassium permanganate (Gulledge and O'Connor, 1973). The rate of oxidation of As(III) to As(V) with oxygen has been found to be very slow at neutral pH values (Ferguson and Gavis, 1972). Under the mildly reducing conditions encountered in most geothermal reservoirs, thermodynamic calculations indicate that arsenic should be present as As(III). The existence of both As(III) and As(V) species under these conditions may be a result of incomplete reduction of arsenate to arsenite, while the existence of both As(III) and As(V) forms in surface waters is probably caused by the slow rate of oxygenation of arsenite to arsenate or bacterial reduction of arsenate to arsenite at neutral pH in localised areas where a reducing environment can exist (Gupta and Chen, 1978).

2.3 Health Effects of Arsenic

Arsenic is a common toxic substance with exceedingly diverse manifestations of poisoning. The toxicity of arsenic species depends on the chemical and physical form of the compound, the route by which it enters the body, the dose and duration of exposure and solubility in biological media (Subramaniam, 1988). The various forms of arsenic, in descending order from most to least toxic, are arsines > arsenites > arsenoxides > arsenates > arsonium compounds > metallic arsenic (Hindmarsh and McCurdy, 1986).

The marked inhibitory effects of As(III) on mitochondrial respiration mediated by NAD-linked substrates appear to play a critical role in the toxicity of this agent. The organic arsenic compounds also react with enzymes containing sulfhydryl groups and inhibit them (WHO, 1981). A recent study has shown that arsenic acts as an endocrine disrupter, upsetting the action of hormones by blocking or mimicking them. These hormones are responsible for turning on many genes that may suppress cancer and regulate blood sugar (Wang, 2001).

The overall response is determined by the magnitude of the exposure dose, but a number of temporal and host susceptibility factors are important modifiers. Long-term exposure to low concentrations of arsenic may cause acute and sub-acute effects on various parts of the body. The major acute effects include gastrointestinal damage, resulting in severe vomiting and diarrhoea, often with blood-tinged stools. Other acute symptoms and signs include muscular cramps, facial oedema, dehydration and cardiac abnormalities. Subacute effects mainly involve the respiratory, gastrointestinal,

cardiovascular, nervous, and haematopoietic systems. Inorganic arsenic is a documented human carcinogen and relatively high incidence of skin and possibly other cancers that increase with dose and age has been observed in populations ingesting water containing high concentrations of arsenic (WHO, 1993).

2.4 Guideline Value for Arsenic in Drinking Water

Data on the association between clinical manifestations and ingestion of arsenic in drinking water are limited and insufficient for a realistic assessment of an exposure-response relationship. Instead, owing to the documented carcinogenicity of arsenic in drinking water in human population, the USEPA has used a multistage model to estimate the lifetime skin cancer risk associated with the ingestion of arsenic in drinking water (USEPA, 1988). On the basis of observations in a population ingesting arsenic-contaminated drinking water, the concentration associated with an excess lifetime skin cancer risk of 10^{-5} has been calculated to be $0.17 \mu\text{g/L}$. This value may, however, overestimate the actual risk of skin cancer as it does not take into account factors such as disease incidence in the population and possible dose-dependent variations in the metabolism that could not be taken into consideration. In addition, this value is below the practical quantification limit of $10 \mu\text{g/L}$. With a view to reducing the concentration of this carcinogenic contaminant in drinking water, the WHO has established a provisional guideline value for arsenic in drinking water of 0.01 mg/L (WHO, 1993).

2.5 Available Methodologies for Removing Arsenic from Water

Various techniques, such as precipitation with iron and aluminium hydroxides, ion exchange, reverse osmosis, and adsorption are employed for removing arsenic from water. The effective removal of arsenic from water requires the complete oxidation of As(III), especially if the drinking water standard is low. All elimination techniques, i.e., adsorption on activated alumina, ion exchange and co-precipitation with ferric or aluminium salts, are effective for As(V) [H_2AsO_4^- , HAsO_4^{2-}], but fail in case of As(III) [H_3AsO_3] (Frank and Clifford, 1986; Jekel, 1994). In natural water, As(III) exists mostly as a hydrophilic, neutral species, arsenous acid (H_3AsO_3 , $\text{pK}_1 = 9.2$), and is not accessible to the major removal mechanisms of anion sorption and anion exchange, whereas As(V) exists as monovalent/divalent anion of arsenic acid (H_3AsO_4 , $\text{pK}_1=2.2$, $\text{pK}_2=7.0$). Although As(III) might be easily oxidised by dissolved oxygen, it persists in aerated waters due to slow oxidation kinetics (Clifford et al., 1983). Therefore, an oxidative treatment of As(III) waters has to be included for effective arsenic removal employing oxidizing agents or suitable catalysts.

Chemical oxidation of As(III) to As(V) by chlorine or potassium permanganate prior to coagulation treatment enhances arsenic removal, indicating that As(V) forms more stable complex with the precipitating metal (Shen, 1973). Ozone also oxidises As(III) even at a dose of 0.1 mg/L but due to its high oxidation potential, it is not feasible for a specific oxidation of As(III). Investigations of the catalytic oxidation with powdered activated carbon showed its principle feasibility for As(III) oxidation, but the oxidation kinetics were slow and the required amount of carbon was rather high

Conventional water treatment involving coagulation, settling and filtration yielded a significant removal of arsenic with the use of ferric sulphate as coagulant (Buswell et al., 1943). Under optimised conditions of ferric sulphate dosage and pH below 7.2, 99% removal of As(V) was obtained, provided the arsenic content of the raw water was below 1 mg/L. Compared to high As(V) removal by ferric salts, As(III) removed was only 50 to 60% (Sorg and Logsdon, 1978). Aluminum salts are in general less effective for both arsenic species, but removal rates of 80 to 90% As(V) are possible in the pH range 6 to 7, where aluminum is itself rather insoluble. The removal of arsenic by the coagulation process is probably due to the complexation of arsenic with polyvalent metals (iron or aluminium) and co-precipitation at the pH value of the metal hydroxide formation (Patterson, 1985).

Lime softening was also found to be an efficient process for arsenic removal. As(V) could be removed by 90% at pH values above 10.5, whereas As(III) could be removed by 75% at pH values above 11.0 (Sorg and Logsdon, 1978). A possible explanation of the mechanism of removal may be adsorption onto the calcium carbonate and magnesium hydroxide, or it may be a direct precipitation of calcium arsenates. Use of powdered bituminous coal additive alongwith lime softening, resulted in a residual arsenic level of 0.05 mg/L at a lime dose of 800 mg/L (pH 11.5) with 2 g/L of powdered coal additive (Dutta and Chaudhuri, 1991).

The use of ion exchange resins for the removal of As(V) has also been

investigated. Due to its different dissociation equilibria, only As(V) will be present as an anion with one or two charges in the medium pH range and can be exchanged in resins. As(V) was found to bound effectively and As(III) passed through a column of anion-exchange resin (Ficklin, 1983; Clifford et al., 1983), and this effect was used to develop a procedure for analytical differentiation of As(III) and As(V). The use of a resin with chelating groups saturated with ferric ions for As(III) and As(V) removal, has also been studied (Yoshida and Ueno, 1978). Both forms of arsenic were effectively removed, but at different optimum pH [pH 3-6 for As(V); pH 8-9 for As(III)].

Amongst the fixed-bed techniques used for removal of arsenic from water, granular activated alumina filtration has been found to be an effective method for arsenic removal as activated alumina is a specific adsorber for anions, and can be regenerated with diluted sodium hydroxide and sulfuric acid (Rosenblum and Clifford, 1984). The optimum pH value for As(V) removal is 5.5 to 6 because at this value, the alumina is protonated, but the anions of the acid added to lower the pH are not yet competitors in adsorption. As(V) is more effectively removed compared to As(III), and oxidation of As(III) to As(V) is necessary to achieve effective arsenic removal (Gupta and Chen, 1978). In field and laboratory studies, alkali-acid pretreated activated alumina has proved very effective in the removal of arsenic from ground water (Fox, 1989; Govind, 1999).

2.6 Potential of Iron and Manganese Oxides in Removing Arsenic from Water

Hydrous iron and manganese and aluminium oxides have been considered to be

the principal solid-phase components controlling the adsorption of arsenic in soils (Yan-Chu, 1994), and these oxides, particularly the redox-sensitive iron and manganese hydroxides under oxidising conditions, constitute significant sinks of arsenic in aquatic systems (Mok and Wai, 1994). Based on the evidence of oxidation of arsenite by iron and manganese oxides, adsorption of arsenite and arsenate by iron hydroxide, and adsorption of arsenate by hydrous manganese oxide (Oscarson et al., 1981a, 1983; Pierce and Moor, 1980, 1982; Takamatsu et al., 1985), it appeared that granular iron or manganese oxide, or a porous supporting medium coated with iron or manganese oxide would serve as an effective medium for removing arsenic from water. Granular ferric hydroxide (Driehaus et al., 1998), iron oxide-coated sand (Joshi and Chaudhuri, 1996) and manganese dioxide-coated sand (Bajpai and Chaudhuri, 1999) media have been developed and found effective in removing arsenic from ground water. However, a redox reaction between iron (III) and As(III) does not occur within 72 h, suggesting that the kinetics of the redox reaction between As(III) and iron (III) is relatively slow; however, manganese oxides are more effective oxidants for As(III) (Oscarson et al., 1981a). Oscarson et al. (1981b) found a first-order reaction rate in the redox reaction of various manganese dioxide (MnO_2) modifications with As(III), and the use of δ - MnO_2 (birnessite) and α - MnO_2 (cryptomelane) led to a faster oxidation of As(III), compared to β - MnO_2 (pyrolusite). They found a substantial lack of release of divalent manganese ions during the oxidation of As(III). According to Takamatsu et al. (1985), accumulation of arsenic in lake sediments results from post-depositional migration of As(III) in the sediment pore water, followed by its oxidation to As(V) by hydrous manganese oxide on the sediment surface and adsorption onto Mn^{2+} -rich hydrous manganese oxide. Driehaus et al. (1995)

observed δ -MnO₂ to be efficient in As(III) oxidation and in adsorbing As(V), and low release of soluble manganese. Borho and Widerer (1996) found manganese dioxide-coated quartz sand from filters removing manganese and iron from ground water to be effective in As(III) oxidation. Thus, a manganese dioxide-based medium would be more effective for oxidation/adsorption of arsenic from water.

In a recent study to examine in detail the oxidation/adsorption of arsenic by manganese dioxide-coated sand, Verma (2000) has reported that the cations present in ground water make the manganese dioxide surface positively charged and thus causing adsorption of As(V) and aiding further oxidation/adsorption of As(III), and that the sand matrix under the coating also plays a role in the adsorption of As(III) and As(V), suggesting that manganese dioxide (δ -MnO₂/ α -MnO₂) coated on a supporting medium with high As(V) adsorption capacity, such as activated alumina, would be a more effective medium for the removal of arsenic from water.

3. SCOPE OF THE PRESENT STUDY

It is evident from the preceding discussion that the arsenic present in ground water may pose a serious threat to human health in many parts of the world where the ground water is the primary source of drinking water. Conventional water treatment methods involving coagulation with hydrolysing metal salts, followed by settling and filtration as well as point-of-use devices based on ion exchange are not feasible for rural areas, because of high cost and skilled operation involved. Methods based on adsorption appear promising because of ease of handling, sludge-free operation and low cost. Activated alumina has proved to be an effective medium for point-of-use treatment for arsenic removal from water. Also, iron oxide- and manganese oxide-based media have been developed – granular ferric hydroxide (Driehaus et al., 1998), iron oxide-coated sand (Joshi and Chaudhuri, 1996) and manganese dioxide-coated sand (Bajpai and Chaudhuri, 1999) – and tested for removal of arsenic from ground water. However, manganese oxides being more effective oxidants for As(III) than iron oxides (Oscarson et al., 1981) and manganese dioxides (δ -MnO₂ and α -MnO₂) being most effective (Oscarson et al., 1981b), a manganese dioxide-based medium would be more effective for oxidation/adsorption of arsenic from ground water. In a recent study to examine in detail the oxidation/adsorption of arsenic by manganese dioxide-coated sand, Verma (2000) has reported that the cations present in ground water make the manganese dioxide surface positively charged and thus causing adsorption of As(V) and aiding further oxidation/adsorption of As(III), and that the sand matrix under the coating also plays a

role in the adsorption of As(III) and As(V), suggesting that manganese dioxide (δ -MnO₂/ α -MnO₂) coated on a supporting medium with high As(V) adsorption capacity, such as activated alumina, would be a more effective medium for the removal of arsenic, As(III) and As(V), from ground water. The present study was undertaken with a view to developing a manganese dioxide-coated activated alumina medium and to examine the removal of arsenic, As(III) and As(V), from ground water by the medium vis-a'-vis removal by activated alumina. The study was conducted along the following lines:

- (a) Preparation of a manganese dioxide-coated activated alumina medium
- (b) A comparative evaluation of the effectiveness of manganese dioxide-coated activated alumina (MDAA) and activated alumina (AA) as a medium for removing As(III) from ground water, employing preliminary column test.
- (c) Examination of the kinetics of arsenic oxidation/adsorption by MDAA and AA, employing batch tests.
- (d) Detailed column test to study the removal of arsenic, As(III) and As(V), from ground water by MDAA vis-a'-vis AA.

4. MATERIALS AND METHODS

4.1 Arsenic-Bearing Water

Water used in the study was I.I.T., Kanpur tap water (a direct ground water supply). An analysis of the water is shown in Table 1. For preliminary column test, the water was spiked with 1.0 mg/L of As(III), using sodium arsenite (NaAsO_2). For studying the kinetics of arsenic removal, the water was spiked with either 1.0 mg/L of As(III), using sodium arsenite (NaAsO_2), or 1.0 mg/L of As(V), using sodium arsenate (Na_2HAsO_4), or 0.6 mg/L of As(III) and 0.4 mg/L of As(V). For the detailed column test, the water was spiked with 1.0 mg/L of arsenic [0.6 mg/L of As(III) and 0.4 mg/L of As(V)]

Table 1 Analysis of I.I.T., Kanpur Tap Water

| | |
|---------------------------------------------------------------|--------------|
| pH | 7.5 - 8.0 |
| Alkalinity, mg CaCO_3 /L | 240 - 250 |
| Hardness, mg CaCO_3 /L | 145 - 195 |
| Calcium, mg CaCO_3 /L | 45 - 70 |
| Magnesium, mg CaCO_3 /L | 100 - 125 |
| Conductivity, $\mu\text{mho}/\text{cm}$ at 25°C | 450 - 550 |
| Phosphate, mg P/L | 0.02 - 0.07 |
| Fluoride, mg F/L | 0.65 - 0.75 |
| Arsenic, mg As/L | Not detected |

4.2 Activated Alumina (AA)

The sample of activated alumina (AA) used in the study was AS-37 (Oxide India Ltd, Durgapur). The characteristics of the activated alumina were: particle size 0.3-0.6 mm, bulk density 0.75-0.85 kg/L and surface area 270.7 m²/g. The activated alumina was subjected to alkali-acid pretreatment - treatment with a 4% sodium hydroxide solution, followed by rinsing with distilled water and subsequent treatment with a 0.5 N hydrochloric acid solution, followed by rinsing with distilled water till the pH of the rinse water was in the range 7.5-8.0.

4.3 Preparation of Manganese Dioxide-Coated Activated Alumina (MDAA)

Manganese dioxide-coated activated alumina (MDAA) was prepared by an incipient wetness impregnation method (Kapteijn et al., 1994). Manganese acetate was used as the precursor for the impregnation to improve the dispersion of manganese dioxide on activated alumina. For the preparation, 2.819 g of manganese acetate $[(CH_3COO)_2Mn \cdot 4H_2O]$ was dissolved in 9.6 mL distilled water. The solution was slowly added to 9.70 g of activated alumina. The sample was dried at 150°C for 3 h, followed by calcination at 400°C for 3 h to form δ -MnO₂ and α -MnO₂. X-ray diffraction (XRD) analysis of the coating confirmed the manganese dioxide coating to be δ -MnO₂ and α -MnO₂. The amount of manganese-dioxide coating was estimated by nitric acid digestion of the coating (Standard Methods, 1995) and by determining the extracted manganese by atomic adsorption spectrometry (Standard Methods, 1995), and it was

found to be 42 mg Mn/g of activated alumina. Surface area of the manganese dioxide-coated activated alumina was 260.8 m²/g.

4.4 Determination of Arsenic

Many methods are available for estimation of arsenic in water but most of them are either unsuitable or tedious for quantitative determination of arsenic at low concentrations. To overcome this problem, arsenic was determined by the molybdenum blue method (Johnson and Pilson, 1972). The method allows for routine analysis of As(III), As(V), and phosphate by spectrophotometric measurement of arsenic- and phosphate-molybdenum blue complexes. Since the water used in the experiment contained negligible amount of phosphate, the method was modified for determination of As(III) and As(V) only. The mixed reagent¹ added to an 'untreated' aliquot of the sample produces a blue color due to the formation of arsenomolybdate complex from any As(V) present. As(III) does not form the complex. Therefore, the intensity of the color formed and hence the absorbance of the 'untreated' aliquot is proportional to the As(V) concentration. Potassium iodate is used as oxidizing agent to convert As(III) to As(V), and hence the absorbance of an 'oxidised' aliquot of the sample is proportional to the total arsenic concentration. As(III) is then calculated as the difference between the total arsenic and As(V). In the procedure, a 40-mL aliquot of the sample was taken into each

¹Mixed reagent (Murphy and Riley, 1962): 125 mL of a 5 N H₂SO₄ and 37.5 mL of a 0.032 M ammonium molybdate [(NH₄)₆Mo₇O₂₄·4H₂O] solutions were mixed thoroughly. Then 75 mL of a 0.1 M ascorbic acid [C₆H₈O₆] solution and 12.5 mL of a 0.0082 M potassium antimonyl tartrate [K(SbO)C₄H₄O₆·4H₂O] solution were added successively with thorough mixing after each addition. This reagent was to be prepared fresh when required.

of four 125-mL erlenmeyer flasks. Two flasks were for 'untreated' and two for 'oxidised' aliquots. One mL of a 1 N hydrochloric acid and two drops of a 50% saturated solution of potassium iodate were added successively to each of the 'oxidised' aliquots, with thorough mixing after each addition. Fifteen min were allowed for oxidation of As(III) to As(V). Thereafter, 4 mL of the mixed reagent were added to each of the 'oxidised' and 'untreated' aliquots, with thorough mixing. This was followed by successive addition of two drops of potassium iodate solution and 1 mL of a 1 N hydrochloric acid solution to each of the 'untreated' aliquots, with thorough mixing after each addition. Then the flasks were placed in a 40°C water bath for 2 h for development of the blue color, following which the absorbance was read in a 40-mm cell at a wavelength of 865 nm. Suitable blanks were run, by the above procedure, along with the samples, and the samples were analyzed in duplicate. $As(III) = (\text{absorbance of 'oxidised' aliquot} - \text{absorbance of 'untreated' aliquot})$ and $As(V) = \text{absorbance of 'untreated' aliquot}$. A standard curve for arsenic was prepared and is shown in Fig. 1. The concentration of phosphate in the water used in the study was 0.02-0.07 mg P/L, and in a recovery experiment [adding a known quantity of As(III) or As(V) to the water and measuring the concentration], up to 0.005 mg/L of As(III) or As(V) could be detected with good precision.

4.5 Preliminary Column Test

Preliminary downflow column test, using 10 mL (8.4 g) of manganese dioxide-coated activated alumina (MDAA) or 10 mL (8.2 g) of activated alumina (AA) medium in a 11 mm ID glass column (medium depth 110 mm) and a flow rate of 1.0 mL/min

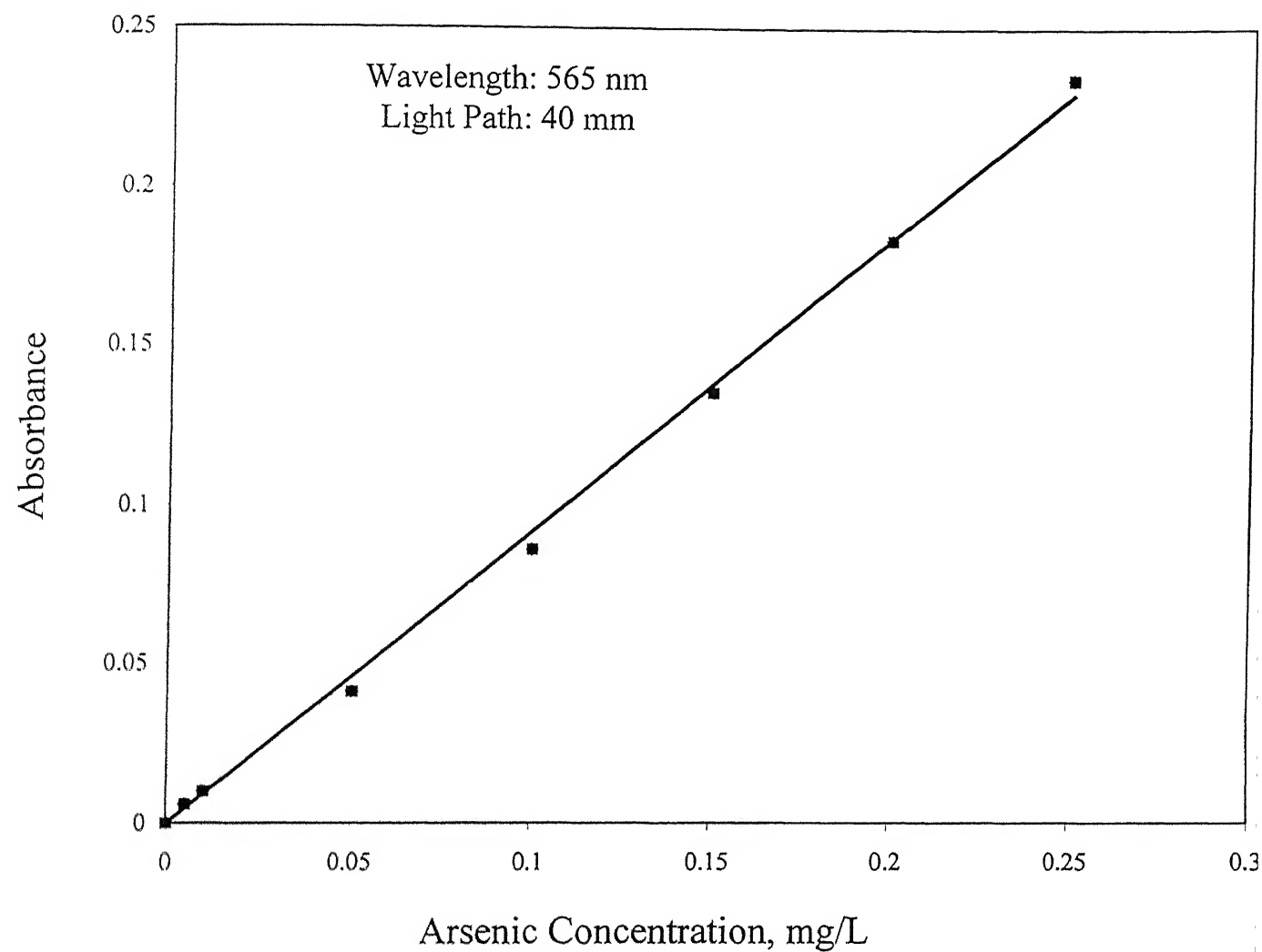


FIG. 1. Standard Curve for Arsenic

(empty bed contact time 10 min), was conducted with the arsenic-bearing [1.0 mg/L of As(III)] water. The column was run until the effluent arsenic exceeded the WHO guideline value of 0.01 mg/L for arsenic in drinking water.

4.6 Batch Test

Batch test was conducted using 100 mL of arsenic-bearing [1.0 mg/L of As(III), or 1.0 mg/L of As(V), or 0.6 mg/L of As(III) and 0.4 mg/L of As(V)] water and 1.0 g of medium (AA or MDAA) in 250-mL glass bottles. The bottles were placed in an end-over-end shaker at 30 rpm, and at predetermined time intervals (5, 15, 30, 60, 90 and 120 min), bottles were withdrawn and the supernatant was filtered through a 0.45- μ m membrane filter, and the filtrate was analysed for residual arsenic.

4.7 Detailed Column Test

Detailed downflow column test, using 63 mL (52 g) of AA or 63 mL (53 g) MDAA medium in a 20 mm ID glass column (medium depth 200 mm) and a flow rate of 3.14 mL/min (empty bed contact time 20 min), was conducted with arsenic-bearing [1.0 mg/L of arsenic (0.6 mg/L of As(III) and 0.4 mg/L of As(V))] water. Before initiating a run, the column was backwashed with distilled water to remove any fine particulate matter. The column was run until the effluent arsenic exceeded the WHO guideline value of 0.01 mg/L for arsenic in drinking water. Following termination of a run, the MDAA medium was regenerated *in situ* by backwashing with 2 L of a 0.2 N sodium hydroxide solution, while the AA medium was regenerated *in situ* by backwashing with 1 L of a 4% sodium hydroxide solution and followed by 1 L of a 0.5 N hydrochloric acid rinse. The

column was then equilibrated by passing distilled water until the influent and effluent pH were identical. Both the spent regenerant and backwash water were collected for three cycles and analysed for the recovered arsenic

5. RESULTS AND DISCUSSION

5.1 Preliminary Column Test

Preliminary downflow column test, using 10 mL (8.4 g) of manganese dioxide-coated activated alumina (MDAA) medium or 10 mL (8.2 g) of activated alumina (AA) medium in a 11 mm ID glass column (medium depth 110 mm) and a flow rate of 1.0 mL/min, was conducted with the arsenic-bearing water [1.0 mg/L of As(III)] for a comparative evaluation of the effectiveness of MDAA and AA as a medium for removing As(III) from ground water. For preliminary column test, ground water spiked with As(III) was taken as As(III) is more toxic than As(V) (Hindmarsh and McCurdy, 1986), and the focus of this study was to develop a more effective medium for As(III) removal as AA is very effective for removing As(V) (Gupta and Chen, 1978; Govind, 1999).

Removal of arsenic by MDAA and AA in the preliminary column test is shown in Fig. 2. Arsenic was detected in the column effluent at 250 and 180 bed volumes for MDAA and AA, respectively. However, breakthrough bed volumes at the WHO guideline value of 0.01 mg/L for arsenic in drinking water were 295 and 230 for MDAA and AA, respectively. The results of the preliminary column test indicates that MDAA is a more effective medium than AA for the removal of As(III). Moreover, the effluent for AA medium was in the form of As(III), suggesting that there was no oxidation of As(III) to As(V) by AA. However, owing to the oxidising properties of δ -MnO₂ and α -MnO₂ (Oscarson et al., 1981b), a portion of the effluent from the MDAA medium was in the

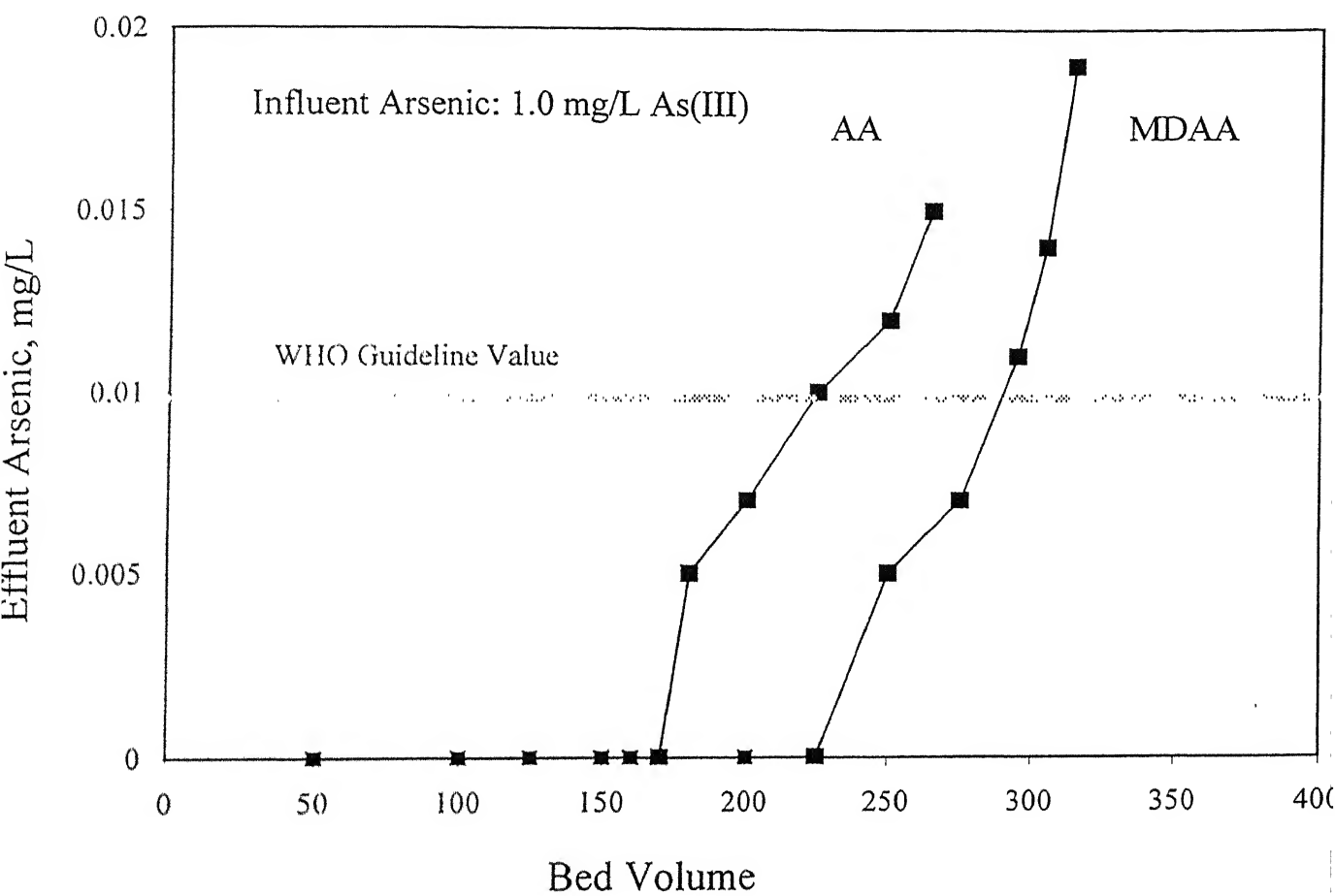


FIG. 2. Arsenic Removal by Activated Alumina (AA) and Manganese Dioxide-Coated Activated Alumina (MDAA) in Preliminary Column Test

form of As(V). To gain further insight into the performance of MDAA and AA for removing arsenic, As(III) and As(V), from ground water, batch tests were conducted

5.2 Batch Test

Batch tests, using 10 g/L of MDAA or AA medium and arsenic-bearing water [1.0 mg/L of As(III) or 1.0 mg/L of As(V) or 0.6 mg/L of As(III) and 0.4 mg/L of As(V)] were conducted to examine the kinetics of arsenic oxidation/adsorption (removal) from ground water by AA and MDAA (Fig. 3).

The variation of arsenic [As(V)] remaining in solution with contact time, for AA and MDAA, are shown in Figs. 3(a) and 3(b), respectively. For this set of batch tests, no As(III) was present initially in the solution. The initial rate of arsenic adsorption onto AA was rapid and 76% removal was achieved in 5 min. Beyond this, adsorption was slower and 99.5% removal was achieved in 120 min. The results are in good agreement with those of Verma (2000), who, under identical conditions, reported approximately 75% removal in 5 min and 96% removal in 120 min. A comparison of Fig. 3(b) with 3(a) shows that the initial rate of arsenic removal is higher for MDAA medium, with 88.5% removal occurring in 5 min and in 60 min nearly complete removal of arsenic was achieved, indicating that both the manganese dioxide and activated alumina matrix removed arsenic and that the cations present in ground water made the manganese dioxide surface positively charged, thus aiding in the adsorption of As(V), which was present in the form of pentavalent anions (HAsO_4^{2-} and H_2AsO_4^-), as observed by Verma (2000). It should be noted that the difference in surface area cannot be the reason for the

higher rate of adsorption by MDAA because the surface area of MDAA is lower than that of AA (refer sections 4.2 – 4.3).

The next set of batch tests were conducted with only As(III) in the solution. The variation of different forms of arsenic remaining in solution with contact time, for AA and MDAA, are shown in Figs. 3(c) and 3(d), respectively. The rate of removal of As(III) by AA was significantly lower than the rate of removal of As(V), with only 38% removal in the first 5 min [Figs. 3(c) and 3(a)]. This lower rate of uptake was due to the fact that As(III) was present as a neutral species (H_3AsO_3), and hence was not as strongly attracted to the positively charged AA surface as the As(V) species (H_2AsO_4^- and HAsO_4^{2-}). In contrast, for MDAA, both As(III) and As(V) were present in solution [Fig. 3(d)]. The source of As(V) was oxidation of As(III) by manganese dioxide ($\alpha\text{-MnO}_2$ and $\delta\text{-MnO}_2$): $\text{H}_3\text{AsO}_3 + \text{MnO}_2 \rightleftharpoons \text{HAsO}_4^{2-} + \text{Mn}^{2+} + \text{H}_2\text{O}$ (Oscarson et al., 1981a; Takamatsu et al., 1985), and As(V) produced as a result of As(III) oxidation adsorbed onto MDAA. Oscarson et al. (1983) and Driehaus et al. (1995) found a substantial lack of release of Mn^{2+} ions during the oxidation of As(III). This lack of manganese release can be attributed to the high adsorption capacity of manganese oxides for soluble manganese and probably to the formation of an As(V)- Mn^{2+} complex.. The manganese dioxides were reported to adsorb As(V) very quickly (Driehaus et al., 1995) and in this way, the rapid initial decrease of As(III) was an effect of both oxidation and adsorption. Due to this oxidation of As(III) and subsequent adsorption, the rate of uptake of As(III) by MDAA was much higher compared to that by AA. For MDAA, the concentration of As(III) decreased by 78% in 5 min compared to 38% for AA [Figs. 3(d) and 3(c)]. As can be seen from Fig. 3(d), As(V) concentration showed a maxima at 5 min contact time. This

can be explained by simultaneous formation of As(V) from As(III) oxidation and subsequent removal of As(V) by adsorption. Initially, when concentration of As(III) is high, oxidation of As(III) to As(V) on the MDAA surface is rapid and the rate of adsorption is initially lower than the rate of oxidation. With further increase in contact time, concentration of As(III) decreased, thereby reducing formation of As(V) and the rate of adsorption became higher than the rate of formation. Due to release of As(V) into solution, initial decrease in the total arsenic concentration was not significantly different from that of AA (52% as compared to 38% in case of AA) [Figs 3(d) and 3(c)]; with increase in contact time, uptake by MDAA became higher (96% at 120 min) than that by AA (83% at 120 min), due to simultaneous oxidation of As(III) to As(V) and adsorption of As(V)

Another set of batch tests were conducted with 0.6 mg/L of As(III) and 0.4 mg/L of As(V) in solution, and the variation of different forms of arsenic remaining in solution with contact time, for AA and MDAA, are shown in Figs. 3(e) and 3(f), respectively. For AA, the initial rate of total arsenic uptake was intermediate between that obtained when As(III) or As(V) was present alone [Figs. 3(a), 3(c), 3(e)], and the initial rate of adsorption of As(V) and As(III) were lower than the rates when either of the species was present alone. Compared to a reduction of 76% in 5 min when As(V) was present alone, the reduction of As(V) in this case was 62% [Figs. 3(a) and 3(e)]. Similarly, the reduction of As(III) in this case was 33% compared to 38% when As(III) was present alone [Figs. 3(e) and 3(c)]. This was most probably due to mutual hindrance in adsorption. Similarly, the total arsenic concentration after 120 min was in between the concentrations obtained when As(III) or As(V) was present alone in solution. A comparison of Figs. 3(f) and 3(d)

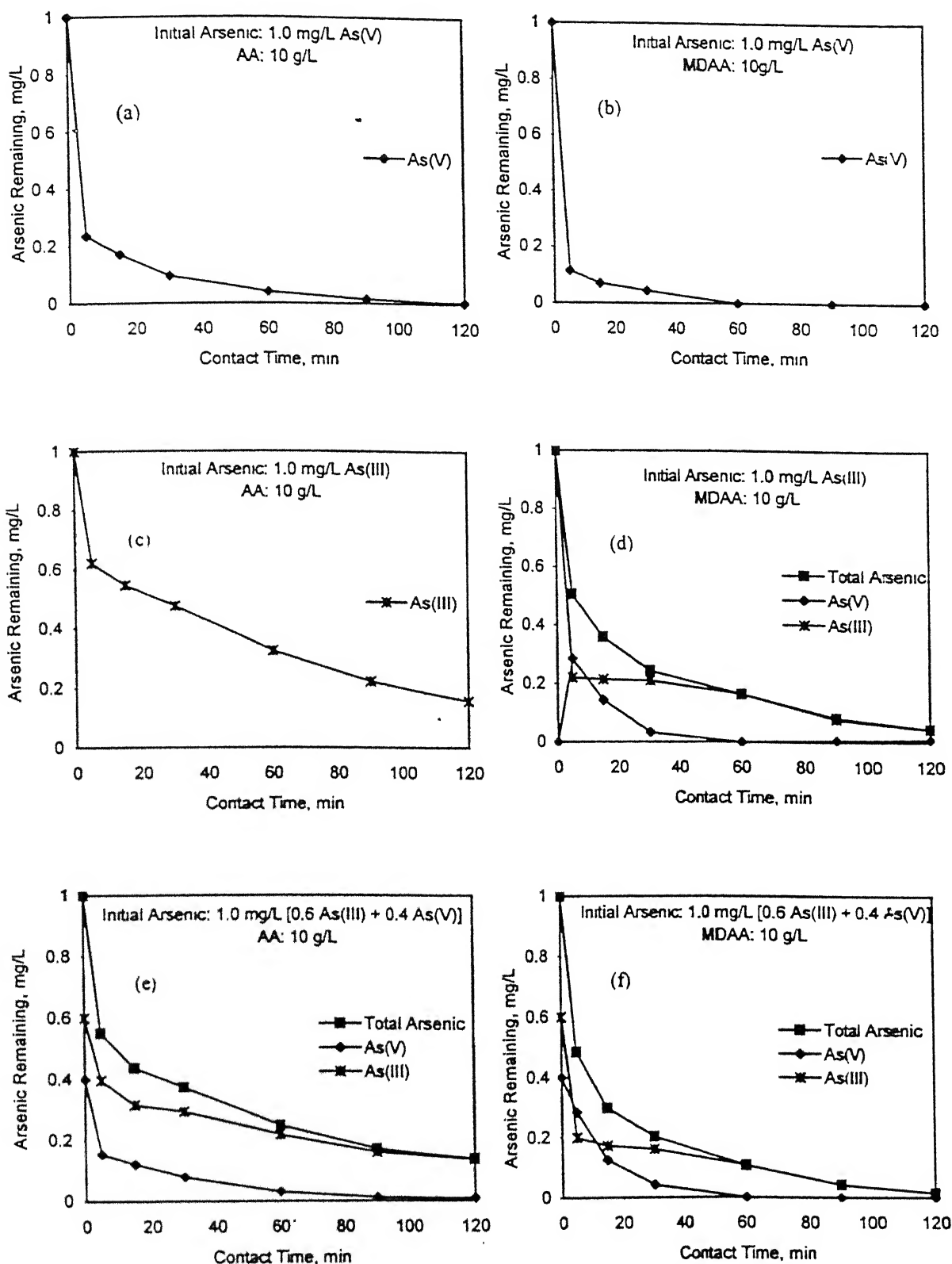


FIG. 3. Kinetics of Arsenic Adsorption/Oxidation by Activated Alumina (AA) and Manganese Dioxide-Coated Activated Alumina (MDAA)

shows that, for MDAA, when both As(III) and As(V) were initially present in solution, no maxima occurred in the variation of As(V) with contact time. Since As(V) was present initially in the system, adsorption of As(V) occurred from the beginning, whereas in the earlier case [Fig. 3(d)], some time was required for the concentration of As(V) to build up before detectable adsorption occurred. Another reason could be relatively lower concentration of As(III), thereby resulting in less formation of As(V) from As(III) oxidation.

5.3 Detailed Column Test

Three cycles of detailed column test, using 63 mL (52 g) of AA or 63 mL (53 g) of MDAA medium in a 20 mm ID glass column (medium depth 200 mm) and a flow rate of 3.14 mL/min (empty bed contact time 20 min), were conducted with arsenic-bearing [1.0 mg/L of arsenic (0.6 mg/L of As(III) and 0.4 mg/L of As(V))] water, to compare the performance of these two mediums for treatment of ground water containing arsenic [As(III) and As(V)] and to assess durability of the MDAA medium. Arsenic removal performance of AA and MDAA are shown in Fig. 4. The total arsenic content and As(III) to As(V) ratio of the influent remained unchanged during all the three cycles. The breakthrough bed volumes at the WHO guideline value of 0.01 mg/L for arsenic in drinking water were in the range 485-580 for AA and 695-825 for MDAA. At the WHO guideline value of 0.01 mg/L for arsenic in drinking water, AA treated 580, 550 and 485 bed volumes in the first, second and third cycles, respectively. The corresponding values for MDAA were 825, 770 and 695 bed volumes, respectively. During regeneration of AA, 88%, 85% and 84% of the arsenic removed were recovered after the three cycles,

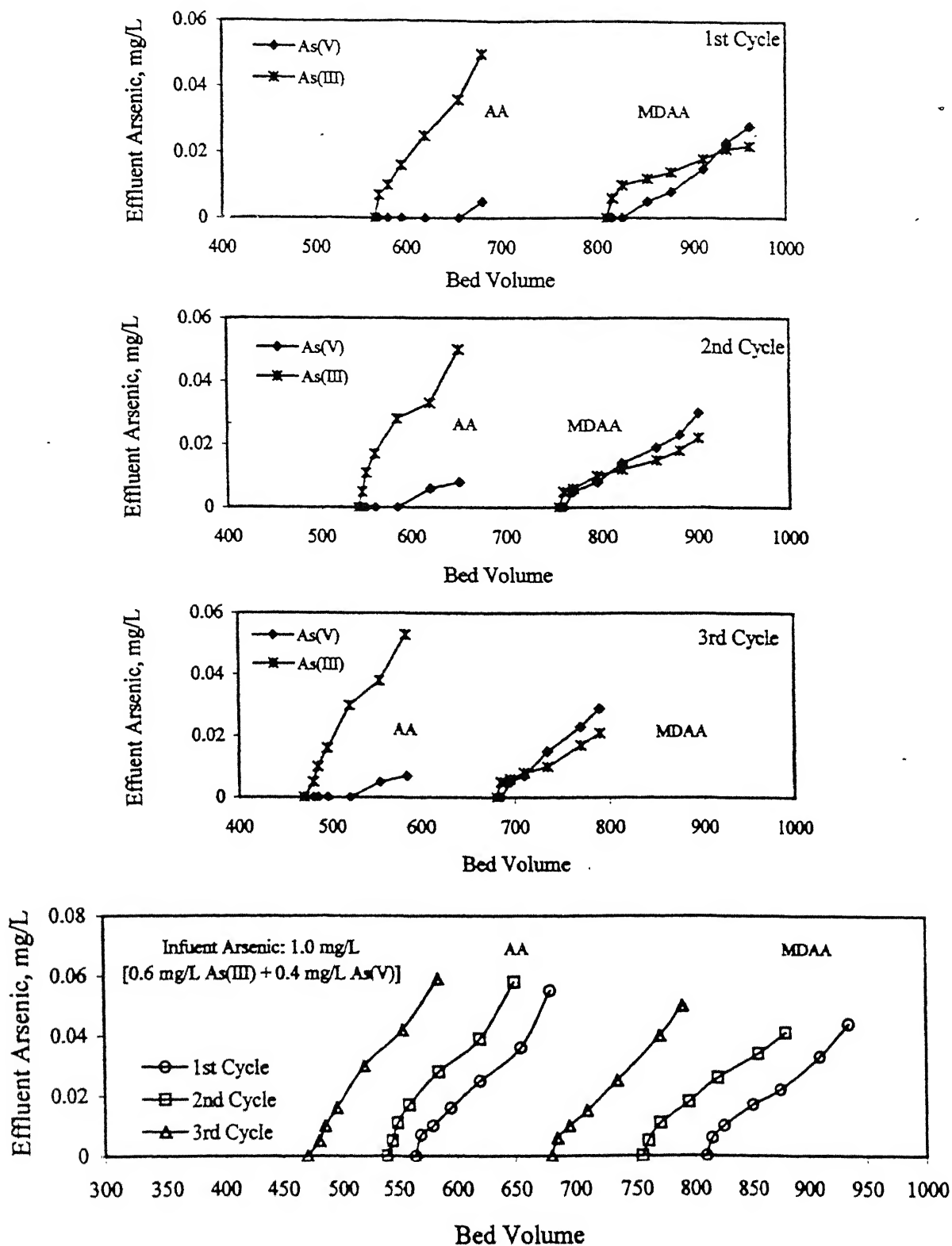


Fig. 4. Arsenic Removal by Activated Alumina (AA) and Manganese Dioxide-Coated Activated Alumina (MDAA) in Detailed Column Test

respectively, whereas for MDAA, 89%, 88% and 86% of the arsenic removed were recovered.

The reason for the higher capacity of MDAA medium for arsenic removal compared to AA medium is that the manganese dioxides (α -MnO₂ and δ -MnO₂) present in the coating oxidise a portion of As(III) to As(V), which is more efficiently adsorbed onto MDAA as the AA present under the manganese dioxide coating is a very effective adsorbent for As(V) (Gupta and Chen, 1978; Govind, 1999). Moreover, the cations present in ground water make the manganese dioxide surface positively charged, thereby aiding in the adsorption of As(V). Due to the oxidation of As(III) to As(V), the effluent from the MDAA column contained both As(III) and As(V) [Figs 4(a), 4(b), 4(c)]. In contrast, for AA, nearly all the effluent was in the form of As(III), and As(V) was detected in the effluent at a point well beyond the WHO guideline value of 0.01 mg/L of arsenic in drinking water.

6. Summary and Suggestions

A manganese dioxide-coated activated alumina (MDAA) medium was developed and removal of arsenic [As(III) and As(V)] from ground water by the medium vis-à-vis their removal by activated alumina (AA) were examined. Batch arsenic removal kinetic tests to examine in detail the removal of As(III) and As(V) from water by AA and MDAA showed that, in comparison to AA, the rates of removal of both As(III) and As(V) were higher for MDAA. In three cycles of downflow column test [medium depth 200 mm; empty bed contact time 20 min; influent arsenic 1.0 mg/L (0.6 mg/L As(III); 0.4 mg/L As(V))] MDAA was found to be a more effective medium for arsenic removal, with breakthrough bed volumes at the WHO guideline value of 0.01 mg/L for arsenic in drinking water being in the range 695-825 for MDAA and 485-580 for AA. The manganese dioxide coating played a role in the oxidation of As(III) to As(V), and both As(III) and As(V) were removed more efficiently by MDAA.

Based on the results of the study, MDAA appeared to be a more effective medium than AA for the removal of arsenic from ground water. More work is required to study the effect of some important factors, such as manganese dioxide loading on AA, water pH, and competing anions and cations on arsenic removal by MDAA. Moreover, efforts are also required to evolve a more cost-effective method of coating as well as medium regeneration, and conduct field tests for assessing the suitability and durability of the MDAA medium.

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